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Hybrid AgNP—TiO_2 thin film based photoanode for dye sensitized solar cell☆

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Summary This article addresses two major issues in the plasmonic dye solar cell; (i) protection of plasmonic nanoparticles from electrolyte attack and (ii) design of appropriate molecular dye to harvest photon near the plasmonic resonance. This report reveals the synthesis of D-π-A carbazole dye and incorporation of plasmonic Ag nanoparticles (AgNPs) into TiO_2 film using Ag—TiO_2 gel. We have designed and synthesized an efficient D-π-A carbazole dye molecule whose absorption maxima matches the plasmonic resonance of AgNPs leading to augmented near field effect, enhancing photon harvesting property of dye molecule. This article also describes a strategy to incorporate AgNPs into the TiO_2 photoelectrode by Ag—TiO_2 gel. The plasmonic photoanode was characterized using SEM and optical spectroscopy. Dye solar cells were characterized by *J—V* characteristics and electrochemical impedance technique in order to take insight into photovoltaic performance and electron transfer kinetic. This engineered DSSC achieves 45% enhancement in current due to the plasmon enhanced near field effect at thin film (3 μm).

Introduction

Plasmonics, a way of manipulating light at the length scale smaller than the wavelength, has been emerged as a curios topic in optics and photonics (Polman and Atwater, 2005). It has been found that when a metallic nanoparticle interacts with the light having wavelength much larger than the size of particle, it generates collective oscillations of valence electrons known as surface plasmon resonance (SPR). Noble metals such as Ag and Au nanoparticles (NPs) are extensively investigated even though the other metals too support plasmon modes. In photovoltaics, plasmonics have enhanced the efficiencies of the devices due to its ability to enhance the light scattering in film (far field effect), near field enhancement by electric field and direct generation of charge

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carriers in semiconductor (Pillai and Green, 2010). Scattered light in the photoeletcrode would allow the light to stay longer in the photoelecrode (increasing the light path through photoelectrode) thereby escalating the probability of light to be harvested by active material.

Many researchers have attempted the fabrication of plasmonic enhanced photoelectrode in DSSC by using naked metallic NPs of Ag and Au and showed the marked enhancement in performance of device (Ding et al., 2011; Dadgoster et al., 2012; Standridge et al., 2009). A report showed that the plasmonic enhanced DSSC requires 62% less material than the conventional DSSC without sacrificing the device performance (Du et al., 2012). Recently emphasis has been given on the direct incorporation of metallic NPs into the photoelectrode thereby improving the near field effect (Muduli et al., 2012; Sebo et al., 2013; Naphade et al., 2014). Our survey shows that the combination of AuNPs with N719 dye gives better results since the absorption of N719 dye and plasmonic peak of AuNPs are in same vicinity (Standridge et al., 2009; Xu et al., 2013) but that of AgNPs are quite apart, so in case of Ag, proper molecular architecture of sensitizer is required.

In this paper the purpose of our study is primarily designing of D-π-A dye to enhance the near field effect. Hence, we have embedded the AgNPs in the TiO_2 matrix by using Ag—TiO_2 gel as precursor which upon sintering fuses with the TiO_2 NPs. This phenomenon will decrease the proximity of metallic nanoparticles and semiconductor thereby giving better near field effect. Further, near field effect has been harvested by designing and selecting the proper D-π-A carbazole based dye molecule whose absorption matches to the plasmonic resonance of NPs. It has been found that the combination of Ag with carbazole based dye yields 45% enhancement in the current.

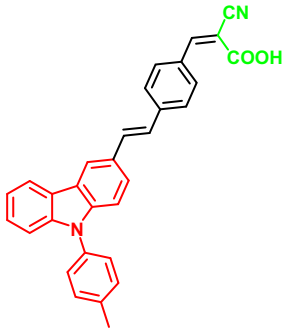
Experimental

Materials and reagents

All the chemicals were purchased from the Sigma—Aldrich and used without further purification. Solvent used for cyclic voltammetry (CV) was purified by following standard protocol. 3-Methoxy propionitrile, guanidiunium thiocyanate, and 4-tert butyl pyridine (4-TBP) having high purity were purchased from the Sigma—Aldrich. FTO glass substrates (7 Ω/cm^2) and hot melt tape were purchased from Solaronix Inc, Switzerland.

Fabrication of plasmonic electrode

TiO_2 functionalized AgNPs were prepared by DMF induced reduction with slight modifications to the reported procedure (Tom et al., 2003). In a typical experiment, a solution containing equimolar (20 mM) amounts of titanium isopropoxide and acetylacetone in 2-propanol was prepared. Another solution of 8 mM $AgNO_3$ and 15 M H_2O in DMF was prepared. A 40 mL sample of the first solution and 25 mL of the second solution were mixed, stirred (20 min) and refluxed for 90 min. So prepared gel was separated by centrifugation and washed thoroughly with ethanol. The obtained Ag—TiO_2 (in gel form after centrifugation and prior to calcinations) particles were directly incorporated into the TiO_2 paste. This paste was applied onto the buffer layer coated (a thin compact layer of TiO_2) TCO substrate using screen printing technique until a desired thickness of 3 μm is achieved. This electrode was finally calcined into the furnace at 450 °C for 20 min.



Scheme 1 Structure of SK 1 dye.

Fabrication of dye solar cell

DSSCs were fabricated using sandwich type configuration of photoelectrode and counter electrode. Dye soaking of the prepared plasmonic electrode and reference electrode was carried by immersing into 0.5 mM solution of SK 1 dye (Barpuzary et al., 2014) (Scheme 1), in ethanol and dichloromethane (1:1 volume ratio) for 18 h.

Counter electrodes were fabricated by spin coating of 50 mM H_2PtCl_6 solution in isopropanol onto predrilled FTO substrate followed by sintering at 450 °C for 15 min. Dye sensitized photo electrode and Pt counter electrode were sealed together using hot melt sealing tape. Electrolyte solution comprises of the 0.5 M LiI, 0.05 M I_2, 0.5 M *tert*-butyl pyridine, 0.5 M guanidium thiocynate in 3-methoxy propionitrile, was inserted through the predrilled holes onto the counter electrode. Holes were sealed using epoxy adhesive and cover glass. Active area of the DSSC was set to 0.2 cm^2 and was maintained constant using the same screen for coating.

Characterizations

SEM was recorded using JSM 7600F FEG-SEM Instrument with accelerating voltage 30 kV. Sample was coated with palladium by vapour deposition in order to generate better contrast in the SEM image. Solar cell performance in terms of PCE was measured using Solartron 1287 interface by sweeping potential from 0 to 0.8 V at a scan rate 20 mV/s under the simulation of white light with intensity 100 mW/cm^2 (AM 1.5). While electrochemical and impedance measurements were carried out using Solartron 1260+1287 interfaces and data were analysed using Corrview and Zplot software (Scribner's Associates Inc.). Impedance of the DSSC was measured by sweeping low amplitude AC signal (10 mV) having frequency ranging from 120 kHz to 0.1 Hz. During the measurement cells were held in dark under the application of 0.6 V DC bias.

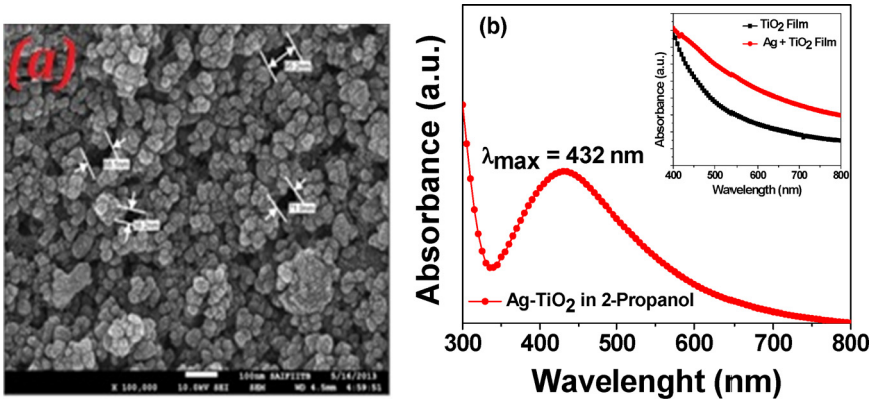


Figure 1 (a) SEM micrograph, (b) optical spectra of Ag—TiO_2 gel.

Results and discussion

AgNPs—TiO_2 photoanode

In order to confirm morphological characters of plasmonic photoanode to insure the porosity of the matrix, SEM study was carried out (Fig. 1(a)). SEM image reveals the nanoporous TiO_2 film with pore size ranging from 40 to 100 nm in plasmonic electrode or bare TiO_2 electrode.

It is well known that the surface plasmon resonance is supported in the high dielectric medium thereby giving change in the optical spectrum of the metallic nanoparticles. An UV—vis spectrum of spherical AgNPs without coating shows a peak with absorption maxima centred at 400—405 nm. This study involves the coating of AgNPs with TiO_2 designing a metal/semiconductor interface since the dielectric of the semiconductor is more than that of metal, plasmon resonance is giving red shift i.e. to 432 nm in our study (Fig. 1(b)). But in our case the shifting of the plasmon mode is more bathochromic than reported by Qi et al. for Ag@TiO_2 particles (Qi et al., 2011). Larger magnitude of shift may be due to the shape effect of plasmonic particles since the transition of spherical to ellipsoidal geometry also shifts the absorption maxima to longer wavelength. This behaviour has been observed by Soni and coworkers in the UV—vis spectroscopy study of AgNPs with different shapes (Soni et al., 2013). Inset of Fig. 1(b) shows the optical absorbance response of the photoanodes. From the figure it is confirmed that incorporation of Ag NPs is enhancing the absorption of photoanode in the visible range.

Characterization of dye sensitized solar cell

Dye sensitized solar cells (DSSC) were fabricated using the photoelectrode sensitized SK 1, D-π-A dye molecule by using TiO_2 as semiconductor, Pt as counter electrode and a liquid electrolyte based on iodide/triiodide. DSSCs were assembled using two photoelectrodes such as Ag—TiO_2 (3 μm thick) and bare TiO_2 (3 μm thick) devices are designated as AT3 and T3 respectively. Fig. 2(a) reveals the *J—V* characteristics of the fabricated solar cells measured at simulated sun light with intensity 100 mW/cm^2 (AM 1.5) and photovoltaic parameters are depicted in Table 1. It has been found from photovoltaic measurements that the incorporation of AgNPs into photoanode leads to the enhancement in current density, fill factor as well as in photovoltage.

Incorporation of the AgNPs into the TiO_2 matrix has led to almost 45% enhancement in the photocurrent while 15% enhancement in the fill factor. But it has been found strange while considering the enhanced photovoltage. Generally the enhanced photovoltage seems to be increased by suppressing the recombination or movement of TiO_2 Fermi level in photoanode. But both these DSSC are having same electrolyte additive hence the magnitude of recombination may

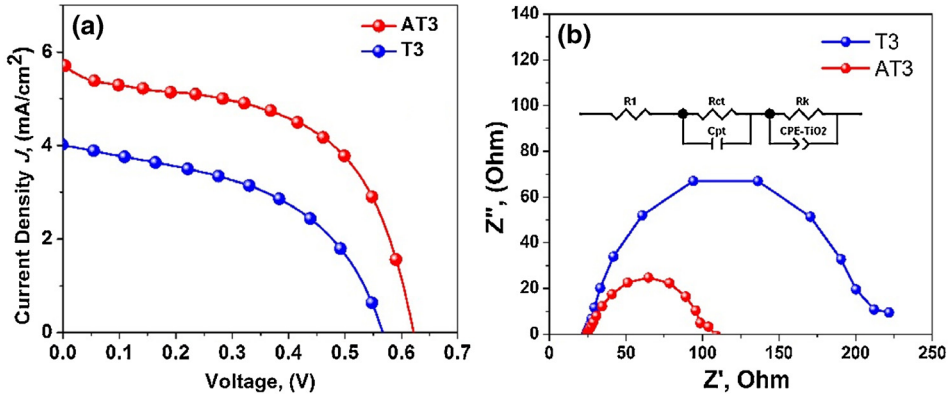


Figure 2 (a) *J—V* and (b) EIS measurements for the DSSC with and without AgNPs.

Table 1 Photovoltaic characterizations and charge transfer parameters of the DSSC.

Device	J_{sc} (mA/cm^2)	V_{oc} (mV)	*FF* (%)	η (%)	R_{ct} (Ohm)[a]	τ_{ele} (s) [a]	R_k (Ohm)[a]	C (μF)[a]	CPE-P[a]
T3	4.0	507	46	1.1	5.5	52	78	102	0.78
AT3	5.7	621	54	1.9	4.8	70	179	60	0.89

J_{sc}: short circuit current density, V_{oc}: open circuit voltage, FF: fill factor and η: efficiency.
[a] Values estimated by fitting Nyquist plot.

be similar. Since the incorporation of the Ag—TiO_2 gel in TiO_2 matrix mimic the function of $TiCl_4$ treatment yielding better contact with TiO_2 particles making better charge transfer through NPs but does not affect V_{oc} (O'Regan et al., 2007). It can be concluded that the incorporation of TiO_2 NPs might have caused the movement of Fermi level leading to enhanced photovoltage. Voltage gain in the plasmonic DSSC suggests that there is less recombination in the device as compared to bare DSSC. To scrutinize the role of AgNPs in the DSSC, electron transfer kinetic of the devices was studied in detail. An insight into the electron transfer kinetic of the devices AT3 and T3 was taken by AC impedance technique in dark under DC bias and the obtained results are depicted in Table 1. EIS data in Fig. 2(b) were represented graphically, and the impedance response was fitted by using widely accepted transmission line model in order to estimate the electron transfer parameters (equivalent circuit is given in inset of Fig. 2(b)).

EIS results reveal that the electron transport property of plasmonic film (device AT3) is quite enhanced as has been reflected by middle arc whose resistance is quite lower than device T3 (without AgNPs). It should be noted that in this figure, the first arc which is attributed to the charge transfer at Pt/electrolyte interface is a depressed semicircle so it cannot be visible perfectly.

Charge transfer resistance was extracted by fitting this semicircle in parallel RC circuit while second arc was fitted using parallel combination of resistance and constant phase element (CPE). Fitting of the second arc yields the recombination resistance and CPE-P (a component of CPE).

It is obvious that the doping of metallic particles into the semiconductor leads to enhancement in the electron density leading to better charge mobility. This same observation is supported by the capacitance value of TiO_2 electrode obtained by approximating second semicircle as combination of parallel resistor and capacitor. Capacitance of plasmonic electrode is almost 45% higher than that of pure TiO_2 based electrode.

Conclusion

In summary, we have demonstrated a new strategy to incorporate the plasmonic NPs in the TiO_2 matrix rendering them less susceptible to leach into the electrolyte along with augmentation of near field effect by plasmonic component using appropriate sensitizer. We have designed an SK 1 dye whose absorption maximum matches to the plasmonic resonance of AgNPs. This combination amplifies the near field in the photoanode thereby leading to better light harvesting property. More than 45% enhancement in the photocurrent along with slight gain in photovoltage was achieved using AgNPs in TiO_2 film sensitized with SK 1 dye.

Conflict of interest

The authors declare that there is no conflict of interest.

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